(12) UK Patent Application (19) GB (11) 2 194 846 (13) A

(43) Application published 16 Mar 1988

(21) Application No 8720705

(22) Date of filing 3 Sep 1987

(30) Priority data
(31) 61/206686 (32) 4 Sep 1986 (33) JP

(71) Applicant
NGK Insulators Ltd.

(Incorporated in Japan)

2–56 Suda-cho, Mizuho-ku, Nagoya City, Aichi Pref, Japan

(72) Inventors
Toru Kodachi
Jun Usami

(74) Agent and/or Address for Service
Mewburn Ellis & Co.,
2/3 Cursitor Street, London EC4A 1BQ

(51) INT CL⁴
G01N 27/56 F23N 5/24

(52) Domestic classification (Edition J):
G1N 19D10 19F1A 19F1B 19F3 19X5 25A1 25C3T 25C4D 25D2 25D6 25DX 25E1 25F7B BKT BPT
U1S 1438 1951 2182 G1N

(56) Documents cited
GB A 2188436 GB A 2188433 EP A2 0138170
GB A 2188435 GB 1594247 EP A2 0068323
GB A 2188434 GB 1577048

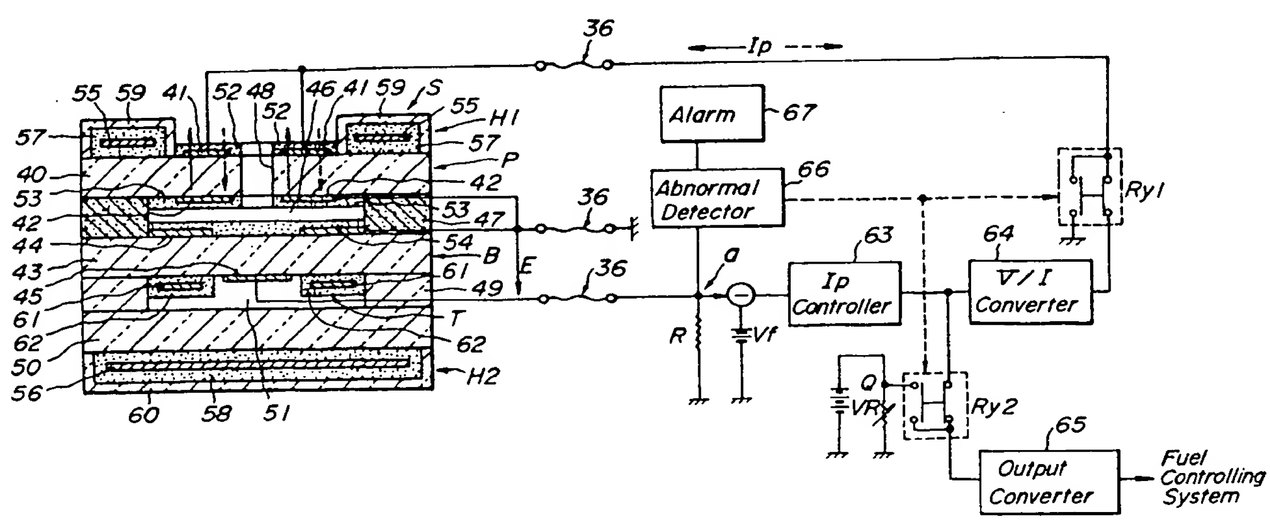
(58) Field of search
G1N
Selected US specifications from IPC sub-classes F23N G01N

(54) Oxygen concentration measuring device

(57) An exhaust oxygen concentration measuring device comprises a diffusion chamber 46 and solid electrolyte to measuring 44,45, and oxygen pumping 41,42 portions. The measurement voltage is composed with a reference voltage V_f and the difference signal is used both to control the pump current via 64 and R_y1 and as an input to the fuel control system. The condition of the measuring device is supervised at 66 by detecting an abnormal condition if the measurement voltage either exceeds a first threshold level or is below a second threshold level.

On detection of an abnormal signal, the pump current is switched off by R_y1 and a backup signal representing a standard oxygen concentration if fed to the fuel control system by R_y2.

FIG_4



GB 2 194 846 A

2194846

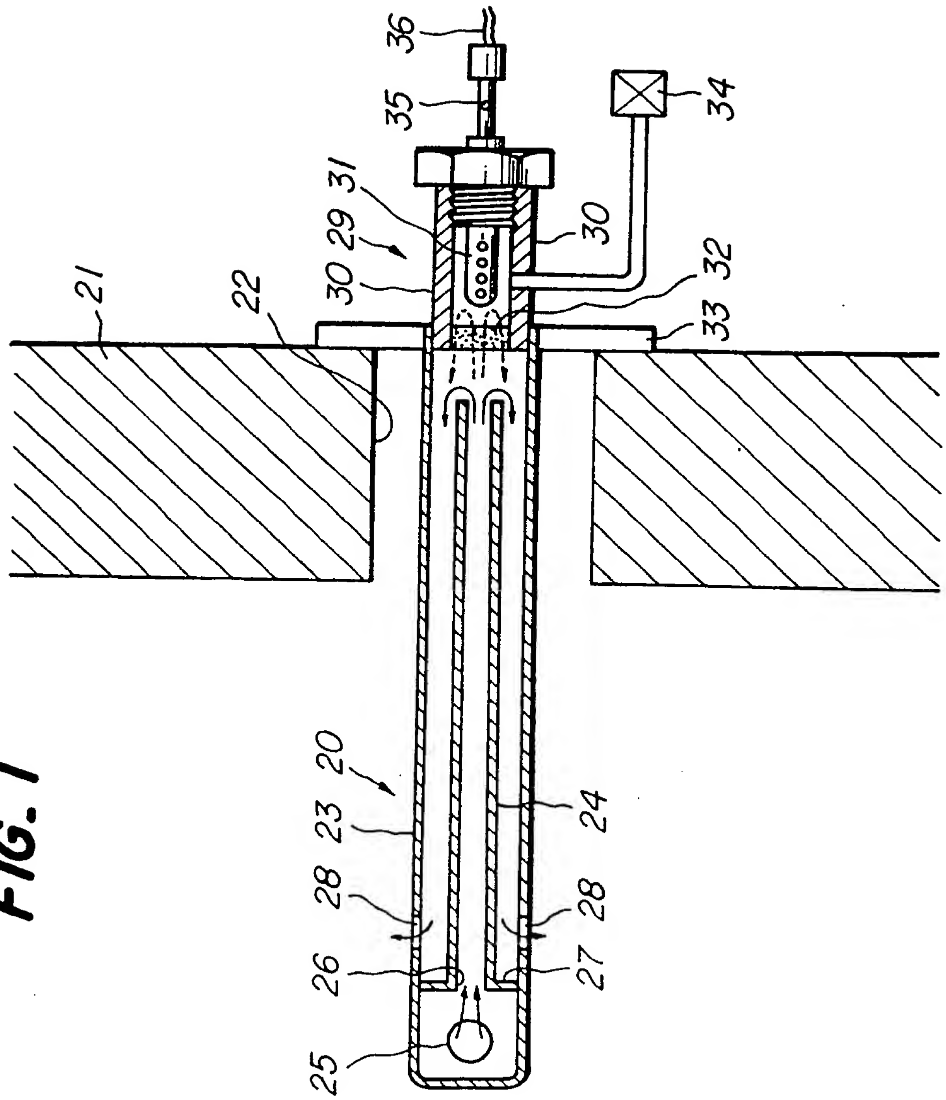


FIG. 1

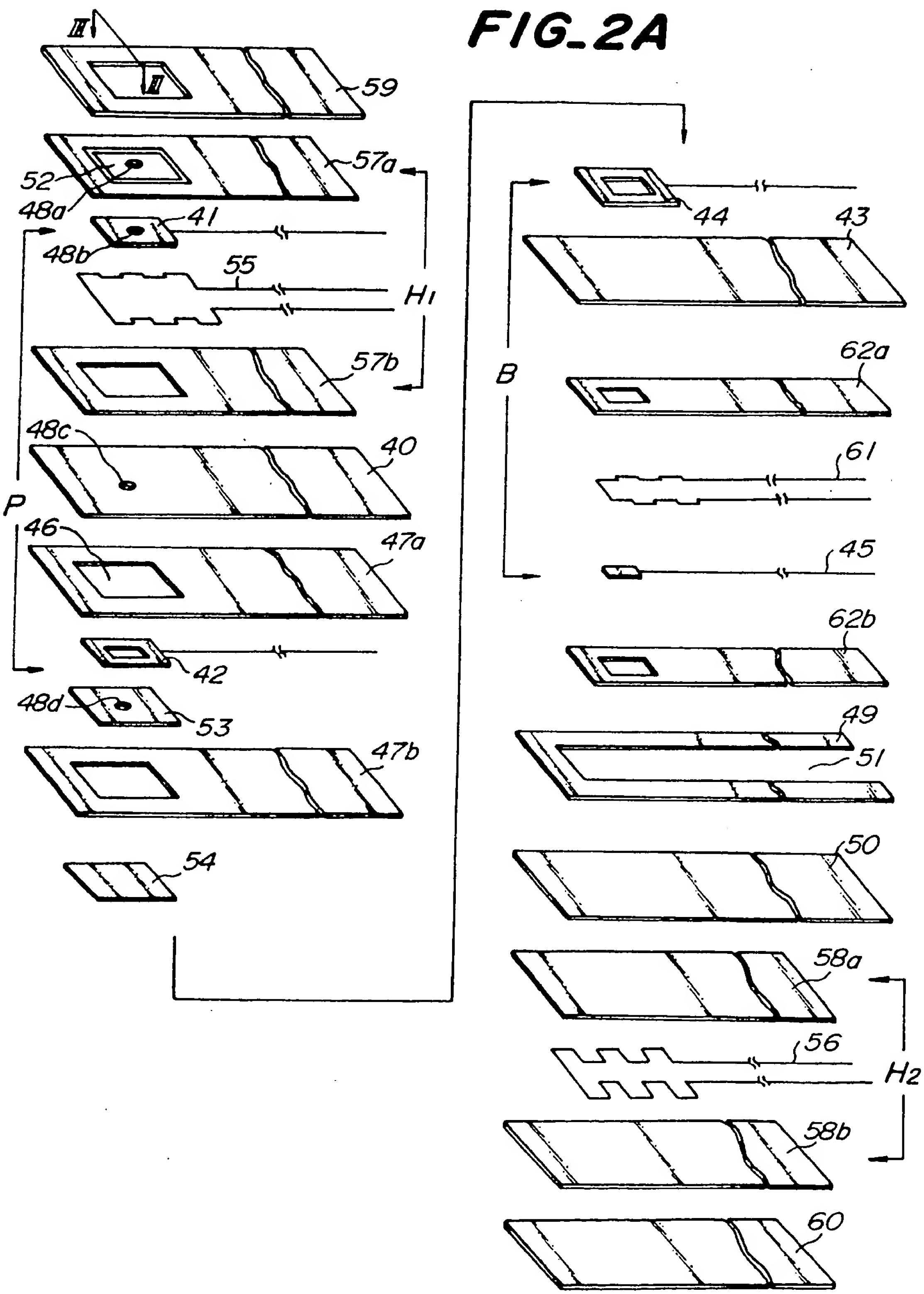
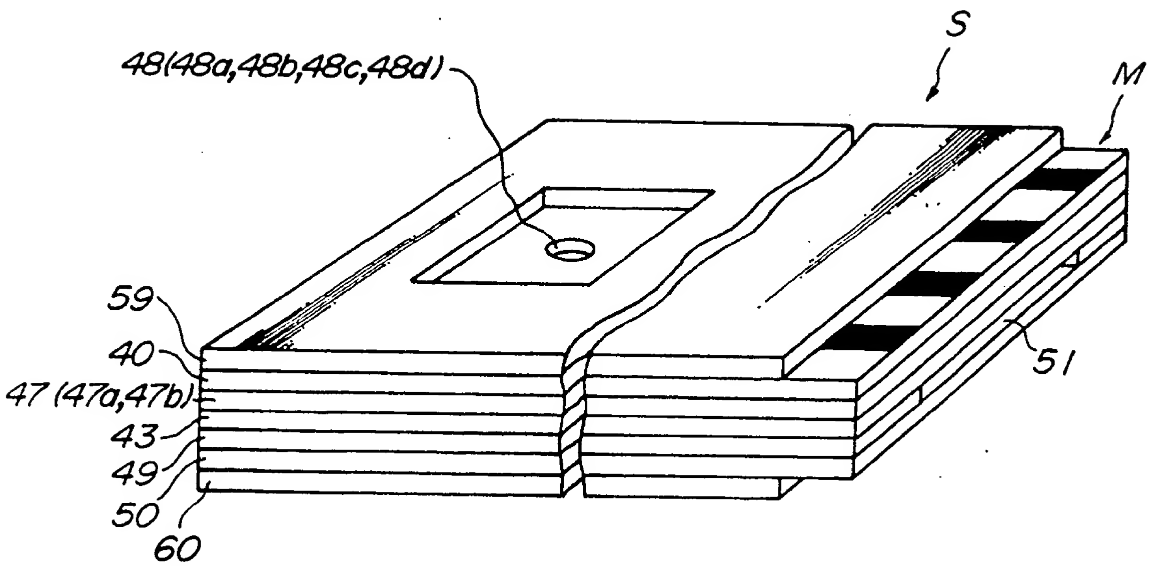

III
III
59
57a
52
48a
41
48b
55
H1
57b
48c
40
P
46
47a
42
48d
53
47b
54
44
43
B
62a
61
45
62b
49
51
50
58a
56
H2
58b
60

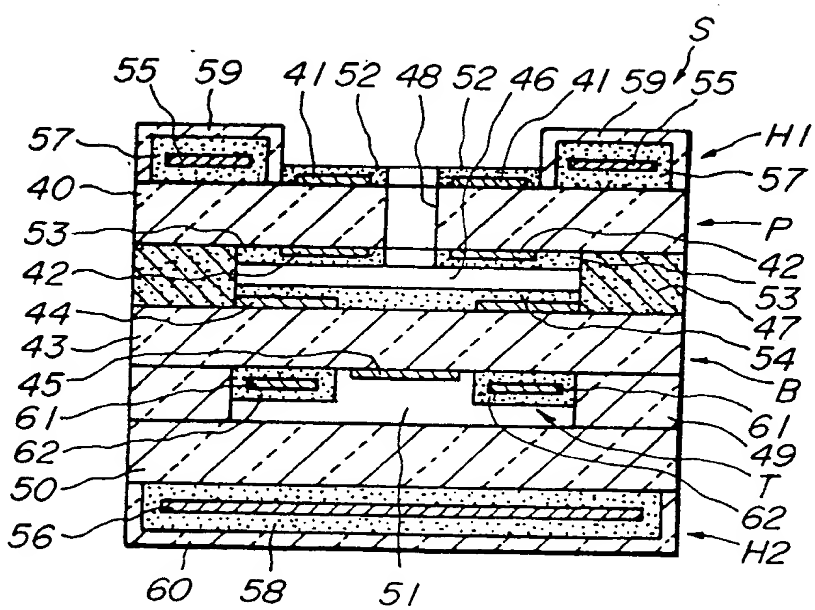
FIG_2A

FIG. 2B



2194846

FIG_3



2194846

FIG. 4

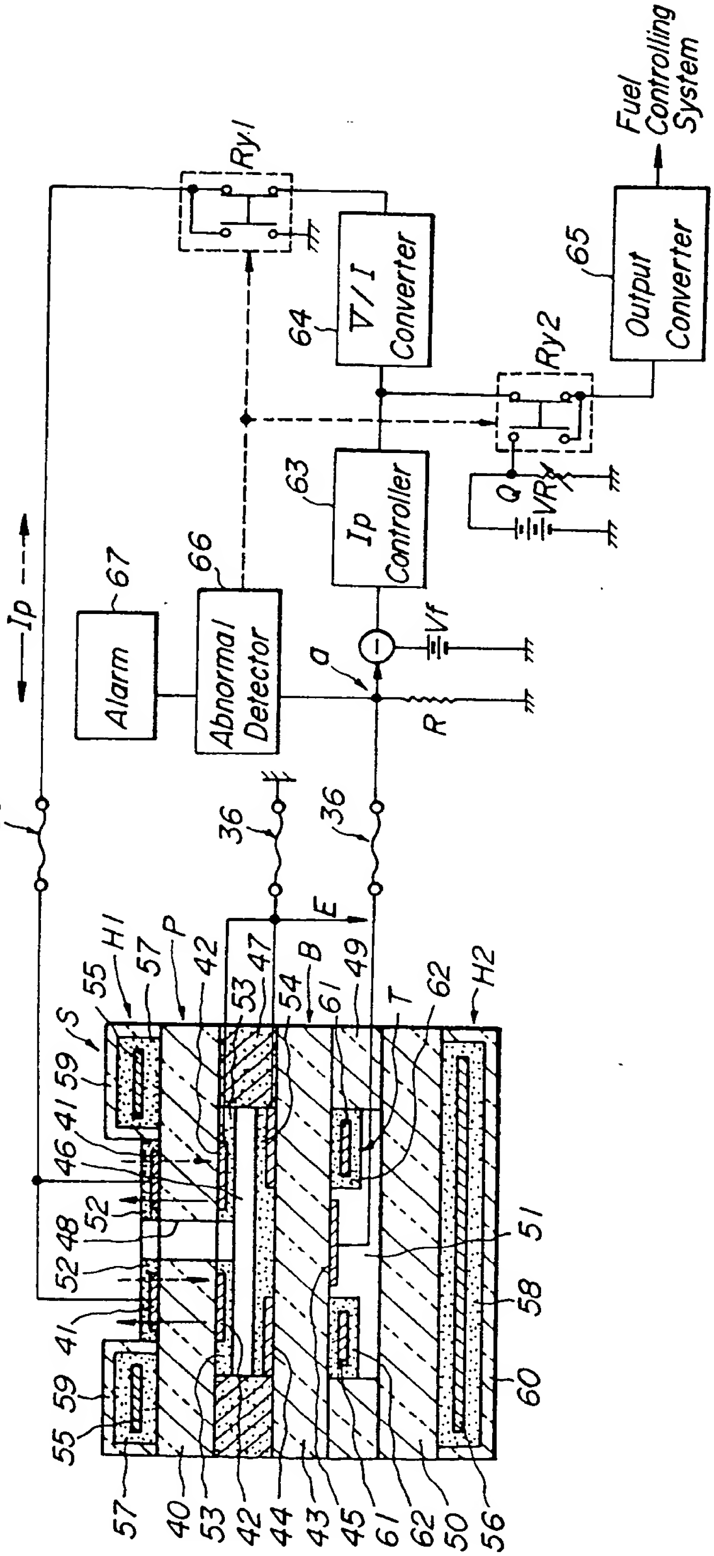
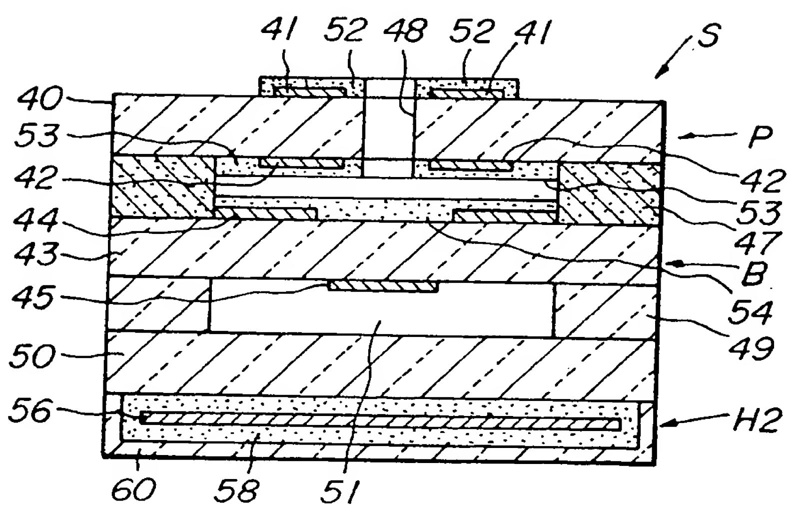


FIG. 5



SPECIFICATION

An oxygen concentration measuring device

The present invention relates to a device for measuring oxygen concentration in the industrial purposes suitable for use in the combustion controlling system of various combustion furnaces or the like. More especially, the invention relates to an oxygen concentration measuring device suitable for use in the measurement of oxygen concentration in a combustion exhaust gas or the measuring gas to detect the oxygen concentration thereof and the device having a self diagnosis function by which when an abnormal condition had happened in the output signal of the detecting portion including an oxygen concentration cell, a suitable countermeasure against the abnormal condition could be dealt with.

In the conventional devices of this kind, a self-diagnosis function is provided by superposing a bias signal on an output signal taken from the electromotive force of an oxygen concentration cell, when the detecting portion is formed only from the oxygen concentration cell. An abnormal condition, for instance, an open wire condition of lead wires leading from the detecting portion to an amplifier or the like is detected by using thus provided bias signal.

In such a known system, no practical counter-measure had been taken, for instance, to control a combustion controlling system of a combustion furnace in safety side after the detection of the abnormal condition based on the signal representing the oxygen concentration of the measuring gas exhausted from such a combustion furnace. Due to this incompleteness of the conventional system, when an abnormal condition like an open wire of the lead wire had happened, an erroneous signal not related to the actual oxygen concentration of the measuring gas is delivered to the output, which shows that the measuring gas, or more practically the combustion exhaust gas from said combustion furnace has high oxygen concentration. Then the combustion of the furnace is controlled according to such an erroneously detected signal. Under the situation, the combustion condition might suddenly jump into an excess fuel condition, which involves a danger of explosion by the excess fuel condition.

The invention has for its object to solve the abovementioned problems in the conventional systems.

In view of the above object, the oxygen concentration measuring device according to the present invention consists in an oxygen concentration measuring device comprising a diffusion chamber in which measuring gas is filled by diffusion, and a detecting portion having an oxygen concentration cell and an oxygen pumping portion arranged to surround the diffusion chamber, wherein an oxygen pumping current of said oxygen pumping portion is so controlled by an output signal derived from the detecting and obtained from an electromotive force in said oxygen concentration cell that the oxygen molecule concentration in said diffusion chamber is set to a predetermined concentration, and a signal in proportion to said oxygen pumping current and representing the oxygen concentration of the measuring gas is supplied to a control system regulating to produce the measuring gas, the device further comprising;

(a) detecting means for detecting abnormal condition in the output signal from the detecting portion,

(b) switching means for switching the signal representing the oxygen concentration fed to the controlling system to a back-up signal for conducting the controlling object to a safe operation when an abnormal condition is detected by said detecting means.

Figs. 1 to 4 show one embodiment of an oxygen concentration measuring device for an industrial use according to the present invention, in which;

Fig. 1 is a cross-sectional view showing the mount of the device;

Fig. 2A and Fig. 2B show detecting portion consisting of an oxygen sensing element in an exploded view and a perspective view showing assembled condition, respectively;

Fig. 3 is a cross-sectional view of the same taken along line III-III of Fig. 2A;

Fig. 4 is a partly block diagram for showing normal operational principle of the device of the invention and also the controlling function under an abnormal condition; and

Fig. 5 is a cross-sectional view showing a modified embodiment of the oxygen sensing element of the present invention.

In order to help better understanding of the invention, one embodiment of the oxygen concentration measuring device will be explained by referring to the accompanying drawings.

Referring to Fig. 1, a probe 20 for collecting the gas to be measured is arranged by inserting it into an opening 22 provided in the furnace wall 21 of a flue of a combustion furnace. The probe 20 is formed in a double tube construction formed of a closed top outer tube 23 and of an open ended inner tube 24. At the side wall of the top end portion of the outer tube 23, a gas introducing hole 25 is opened to face the combustion exhaust gas (gas to be measured) flowing in the flue or the exhaust gas passageway. Said inner tube 24 is arranged in the outer tube 23 in a position that a top side opening 26 of the inner tube 24 is facing to the gas introducing hole 25. The top open end of the inner tube 24 is supported in the outer tube 23 by means of a partition wall 27 which also acts as a supporter. Thus the inside of the inner tube 24 is separated from the space between the inner tube 23 and the outer tube 24. A

gas outlet hole 28 is provided on the outer tube 23 at a location near the partition 27 but locating towards the base side of the outer tube 23 where the inside of the tube shows negative pressure against the combustion exhaust gas (gas to be measured). According to this construction, the combustion exhaust gas in the flue or the gas to be measured (hereinafter simply termed as measuring gas) collected through the gas introducing hole 25 flows as shown by the arrow marks at first the inside space of the inner tube 23 and then through the space formed between the inner tube and the outer tube and finally exhausted through the gas outlet hole 28.

Furthermore, at the base portion of the probe 20, a gas detecting member 29 is mounted. This gas detecting member 29 is constituted from a cylinder portion 30 provided to communicate with the probe 20, a detecting portion 31 inserted from the right hand base side of the cylinder portion 30 to project in the inner space thereof and fixed by thread coupling thereto and covered by a protecting cap, and a ceramic filter portion 32 provided at the top of the cylinder portion 30 to supply the flowing measuring gas in the probe 20 to the detecting portion 31 after filtering it. The probe 20 and the gas detecting member 29 are jointly fixed to the furnace wall 21 by a flange 33. A calibration gas supplier 34 is attached on the cylinder portion 30 to supply the calibration gas to the gas detecting member 29. An air hole 35 for supplying the reference air to the detecting portion 31 is also provided and also lead wires 36 are provided to derive the detected signal from the detecting portion 31 outwardly.

The construction of an oxygen sensing element S of the oxygen concentration measuring device according to the present invention will be explained by referring to Figs. 2A, 2B and 3. The actual size of this oxygen sensing element S is about 5 mm in width, about 1.5 mm in thickness and about 30-60 mm in length.

At upper side of this oxygen sensing element S generally shown in Fig. 2B, there is provided an oxygen pumping portion P comprising a solid electrolyte element 40, and an upper pumping electrode 41 and a lower pumping electrode 42 being arranged at upper and lower sides of this solid electrolyte element 40. Over the upper surface of this oxygen pumping portion P, an upper heater member H1 is provided to surround periphery of the upper pumping electrode 41.

In a similar manner as the abovementioned oxygen pumping portion P, an oxygen concentration cell portion B is provided. This oxygen concentration cell portion B comprises a solid electrolyte member 43 and a measuring electrode 44 and a reference electrode 45 provided at upper and lower sides of the solid electrolyte member 43 respectively.

Between these oxygen pumping portion P and the oxygen concentration cell portion B, a spacer member 47 (47a, 47b) formed of an insulator having a certain thickness is interposed to form a diffusion chamber 46 in the shape of a narrow flat space to which the measuring gas is introduced with a predetermined diffusion resistance. At the center position of this diffusion chamber 46 in the oxygen pumping portion P, a gas introducing hole 48 (48a, 48b, 48c, 48d) is provided for coupling said diffusion chamber 46 to the outer space, for instance to the measuring location, in which the measuring gas may exist. Accordingly, the measuring gas is introduced through this gas introducing hole 48 (48a, 48b, 48c, 48d) and diffused in the diffusion chamber 46 under a certain diffusion resistance and becomes in contact with the pumping electrode 42 located at lower side of the oxygen pumping portion P. The gas also comes in contact with the measuring electrode 44 of the oxygen concentration cell portion B at the location near said lower pumping electrode 42.

Underneath the oxygen concentration cell portion B, there are provided a spacer member 49 formed of a solid electrolyte and a solid electrolyte member 50 in this order. By this construction, an air passageway 51 is formed in which said reference electrode 45 is exposed. This air passageway 51 communicates with the outer atmosphere at the base portion of the oxygen sensing element S. The abovementioned reference air, in this case the atmospheric air, is introduced in the element through this air passageway 51 and comes in contact with said reference electrode 45.

In the air passageway 51, at a location below the lower surface of the solid electrolyte member 43 and in the proximity of both extremities of the reference electrode 45, a temperature detecting portion T (not shown) is provided.

At further lower side, a lower heater member H2 is provided. By means of this lower heater member H2, together with the upper heater member H1 arranged at either sides of the oxygen pumping portion P and the oxygen concentration cell portion B, the two portions P and B may be heated up to predetermined temperature (for instance over 600°C) from both sides in sandwich like manner.

The solid electrolyte members 40, 43, 50 and the spacer member 49 are made of stabilized or partially stabilized zirconia ceramics which shows oxygen ion conductivity at high temperature. As is known in the art, this stabilized or partially stabilized zirconia ceramics may be obtained by forming solid solution of zirconium oxide with yttrium oxide or calcium oxide etc. Each of the electrodes 41, 42, 44, 45 is formed of porous platinum etc. Among the electrodes 41, 42, 44, 45, the upper pumping electrode 41, the lower pumping

electrode 42 and the measuring electrode 44 being arranged to contact with the measuring gas are applied with porous ceramic layers 52, 53, 54 made of alumina etc. respectively in laminated construction. The measuring gas comes in contact with the electrodes 41, 42, 44 through such porous ceramic layers 52, 53, 54, respectively.

The heater members H1 and H2 are formed of heater elements 55 and 56 being the heating elements covered by porous layers 57 (57a, 57b) and 58 (58a, 58b) respectively formed of alumina etc. having electric insulating feature. Over these porous layers 57 (57a, 57b) and 58 (58a, 58b), air tight layers 59 and 60 are provided respectively formed of solid electrolyte such as zirconia etc. By this, the two heater elements 55 and 56 may be separated or isolated from the outer measuring gas. The heater elements 55 and 56 may be formed, for instance, by printing using paste having the main content of mixture of alumina powder and platinum powder or by arranging cermet like film on the base.

Said temperature detector portion T is constructed by using a resistor body having positive or negative temperature coefficient varying the electric resistance greatly by the temperature variation. A temperature detecting element 61 is embedded in an electric insulative porous layer 62 formed alumina or the like so that the element 61 is electrically insulated from the surrounding solid electrolyte member 43 and the spacer member 49. The resistive body of this temperature detecting element 61 is formed by laminated printing technics using paste having the main content of powder of zirconia, alumina and the like and platinum powder, or paste having the main content of ceramic powder of ceramic, zirconia, alumina etc. and platinum powder added with about 0.1-0.5% of titanium oxide, or paste having the main content of ceramic powder like cermet, zirconia, or alumina etc. added with oxides of manganese, cobalt, nickel etc., or paste having intentionally high temperature coefficient like cermet. It may also be obtained by arranging cermet like film and the like. The resistive body of the temperature detecting element 61 may be formed by a zirconia porcelain, or a platinum wire or platinum film etc. For forming the laminated print of such platinum wire or platinum thin film, the known techniques of CVD, vapour deposition or sputtering may be used. Instead of using resistive body for the temperature detecting element 61, a combination of different kind of metals or pastes or cermets containing each such different kind of metals can be used to form laminated printed circuit of thermocouple body to be used in the temperature detecting element 61.

The abovementioned oxygen pumping portion P, the oxygen concentration cell portion B, the heater members H1 and H2, the temperature detecting portion T and the spacer member 47 are laminated to form a narrow width plate shaped elongated body and then sintered to form a unitary construction. In Fig. 2B, M designates a printed electric contact terminal for the pumping electrodes 41 and 42, for the measuring electrode 44, for the reference electrode 45, for the heater elements 55 and 56, and for the temperature detecting element.

When measuring the oxygen concentration, the oxygen sensing element S or more precisely the oxygen pumping portion P and the oxygen concentration cell portion B are maintained at a predetermined temperature while observing the actual temperature detected by the temperature detecting element 61 of the temperature detecting portion T by conducting a heating current through the heater elements 55 and 56 of the heater portions H1 and H2. In a condition that the oxygen pumping portion P and the oxygen concentration cell portion B are maintained at a certain predetermined temperature for instance, 600°C or that the pre-determined temperature is reached, the measurement process can be started. It takes about 3 minutes in a practical embodiment of the oxygen sensing element S from the beginning of conduction of the heating current to reach the predetermined temperature. The power consumption is about 8 W.

The principle of the oxygen concentration measurement by using the sensing element S will be explained at first by referring to partial block diagram shown in Fig. 4. Thereafter, the function of the device of the present invention when some abnormal condition had happend in the output signal derived from said sensing element S will be explained.

By a comparison of the measuring gas diffused into the diffusion chamber 46 through the gas introducing hole 48 of the oxygen pumping portion P with the reference air in the atmosphere by means of the oxygen concentration cell portion B, an electromotive force E corresponding to the ratio of oxygen partial pressure thereof is produced between the measuring electrode 44 and the reference electrode 45. This produced electromotive force is compared with a comparison voltage V_f (produced electromotive force corresponding to air ratio $m \simeq 1$). A difference voltage ($E-V_f$) therebetween is supplied to an oxygen pumping current (I_p) controller 63.

This pumping current (I_p) controller 63 acts to control the oxygen pumping current (I_p) according to the difference voltage ($E-V_f$), in the following manner.

i) In case of $E<V_f$;

By the regulation of the oxygen pumping current (I_p), the oxygen pumping portion P acts to subtract the oxygen in the diffusion chamber 46 outwardly as shown by the full line shown in Fig. 4.

ii) In case of $E<V_f$;

By the regulation of the oxygen pumping current (I_p), the oxygen pumping portion P acts to introduce the oxygen into the diffusion chamber by the electrolysis decomposition of the carbon dioxide (CO_2) and the water (H_2O) content in the measuring gas as shown by the dotted line in Fig. 4. In the diffusion chamber 46, the reaction is as follows:

$$H_2O+\tfrac{1}{2}O_2 \rightarrow H_2O,\ CO+\tfrac{1}{2}O_2 \rightarrow CO_2$$

By this regulation, the oxygen concentration in the diffusion chamber is controlled to be a predetermined value.

The setting of this predetermined value of the oxygen concentration is so adjusted that the oxygen concentration in the diffusion chamber 46 becomes a value corresponding to air ratio $m \cong 1$, or more practically the oxygen concentration becomes 0%.

Each of oxygen molecule, carbon dioxide molecule, hydrogen molecule in the measuring gas has different diffusion coefficient against that of nitrogen so that the oxygen pumping current (I_p) may be expressed by the following equation:

$$I_p = K_1 \cdot P_{O2} - K_2 \cdot P_{CO} - K_3 \cdot P_{H2}$$

wherein,

K_1 : coefficient in proportion to the diffusion of oxygen molecule.

K_2 : coefficient in proportion to the diffusion of carbon monoxide.

K_3 : coefficient in proportion to the diffusion of hydrogen.

P : respective partial pressure of oxygen molecule, carbon monoxide molecule, hydrogen molecule.

Accordingly, when the measuring gas is in the oxidation region, as the concentration of carbon monoxide molecule and that of hydrogen molecule are both 0%, the following is obtained.

$$I_p = K_1 \cdot P_{O2}$$

When the measuring gas is in the reducing region, as the concentration of oxygen molecule is 0%, the following is established.

$$I_p = -(K_2 \cdot P_{CO} + K_3 \cdot P_{H2})$$

In summarizing the above explained principle of the measurement of the oxygen concentration, the measurement of the oxygen concentration is carried out to control the oxygen pumping current (I_p) so that the oxygen molecule concentration in the diffusion chamber 46 becomes 0% (air ratio $m \cong 1$) and the oxygen pumping current (I_p) is measured through a reference resistance (r_r).

By this, the oxygen exceeding concentration in the oxidation region and the oxygen shortage concentration in the reducing region can be expressed by a single signal. This will greatly contribute for the formation of a controlling system of atmosphere control of an industrial furnace operating in both the oxidation and reducing regions.

Hereinafter, explanation will be given for a case when abnormal condition had happened in the signal derived from the abovementioned oxygen sensing element S.

When the oxygen sensing element S is working properly, more precisely, when no failure or breakage is existing in the oxygen concentration cell portion B and in the oxygen pumping portion B, thus these portions are working normally and if there is no trouble like open wire in the lead wires 36, the produced electromotive force in the oxygen concentration cell portion B will assume voltage value between 300 mV and 500 mV and this voltage appears at point *a* in the circuit shown in Fig. 4.

Whereas, if there is a failure, a breakage or the like in the oxygen concentration cell portion B and/or oxygen pumping portion B or in the lead wires 36 or the like, the following voltage value will appear at said point *a*.

(1) When there is a trouble or breakdown in the oxygen concentration cell portion B, or an open connection in the lead wire extending from the oxygen concentration cell portion B, 0 mV appears at the point *a* through a resistor R connected to the ground.

(2) When there is no trouble nor breakdown in the oxygen concentration cell portion B, and also there is no open connection in the lead wire extending from the oxygen concentration cell portion B, a failure of function or breakage had happened in the oxygen pumping portion P, or if there is an open connection in the lead wires extending from the oxygen pumping portion P;

① if the measuring gas is a combustion exhaust gas burning at the air ratio $m>1$, a voltage below 200 mV appears at the point *a*, and

② if the measuring gas is a combustion exhaust gas burning at the air ratio $m<1$, a voltage above 600 mV appears at the point *a*.

Accordingly, the voltage value of the point *a* is always supervised for the normal condition of the device for the voltage value lying between 200 mV and 600 mV by an abnormal detector 66 formed essentially of a comparison circuit. When the voltage value of the point *a* assumes other than the range between 200 mV and 600 mV, or in other words when a failure or the like as explained in the foregoing had happened, this abnormal detector 66 energizes a first relay R_y1 for interrupting the oxygen pumping current (I_p), and a second relay R_y2 for supplying a back-up signal Q having a predetermined value through its switching contacts to the output converter 65. Also an alarm circuit 67 is energized by the

abnormal detector 66 for indicating alarm signal. The above back-up signal Q is set to be a voltage signal value to promote excess air burning condition in the combustion furnace by a combustion control system and to extinguish the combustion eventually. This voltage signal value can be varied freely by a variable resistor VR included in a control circuit connected to a contact terminal of the second relay R_y2.

As has been explained in the foregoing, since the oxygen pumping current (I_p) is interrupted when an abnormal condition is detected, the breakdown of the oxygen pumping portion P itself by an extraordinary amount of flow of the oxygen pumping current (I_p) can be prevented. Furthermore, by the above explained switching to the back-up signal Q, a danger of explosion by the burning under excess fuel condition is prevented definitely and the total combustion system is conducted into a safety operating furnace combusting under oxygen excess condition.

A modified embodiment of the oxygen sensing element S will be explained by referring to Fig. 5, in which the same parts are indicated by the same reference numerals and a duplicated explanation is omitted.

This embodiment is almost identical to that shown in Fig. 3 except that the upper heater portion H1 and the temperature detecting portion T are removed. In this modified embodiment, the temperature of the oxygen sensing element S is detected by using the variation of resistance value of the heater element 56 of the lower heater portion H2 and the temperature control is effected. All the other portions are identical with those of the previous embodiment.

In accordance with the present invention, the combustion system or the object to be controlled is automatically conducted into a safely operating combustion system by the detection of occurrence of the abnormal condition and by the supply of the back-up signal and the safe operation of the controlling system is thus assured.

CLAIMS

1. An oxygen concentration measuring device comprising a diffusion chamber in which measuring gas is filled by diffusion, and a detecting portion having an oxygen concentration cell and an oxygen pumping portion arranged to surround the diffusion chamber, wherein an oxygen pumping current of said oxygen pumping portion is so controlled by an output signal derived from the detecting portion and obtained from an electro-motive force in said oxygen concentration cell that the oxygen molecule concentration in said diffusion chamber is set to a predetermined value of concentration, and a signal in proportion to said oxygen pumping current and representing the oxygen concentration of the measuring gas is supplied to a control system regulating to produce the measuring gas,

the device further comprising;

(a) detecting means for detecting abnormal condition in the output signal from the detecting portion,

(b) switching means for switching the signal representing the oxygen concentration fed to the controlling system to a back-up signal for conducting the controlling object to a safe operation when an abnormal condition is detected by said detecting means.

2. An oxygen concentration measuring device as claimed in claim 1, wherein the device further comprising interrupting means for interrupting the oxygen pumping current when an abnormal condition is detected by the detecting means.

3. An oxygen concentration measuring device as claimed in claim 1 or 2, wherein the predetermined value of the back-up signal can be varied freely.

4. An oxygen concentration measuring device as claimed in claim 1, 2 or 3, wherein an abnormal alarm is energized when an abnormal condition is detected by the detecting means.

5. An oxygen concentration measuring device substantially as herein described with reference to and as shown in Figs. 1 to 4 of the accompanying drawings or Fig. 5 of the accompanying drawings.

Published 1988 at The Patent Office, State House, 66/71 High Holborn, London WC1R 4TP. Further copies may be obtained from The Patent Office, Sales Branch, St Mary Cray, Orpington, Kent BR5 3RD. Printed by Burgess & Son (Abingdon) Ltd. Con. 1/87.